ABSTRACTS OF THE PHYSICO-CHEMICAL LITERATURE IN JAPAN

Vol. XIII **December, 1939** **No. 3**

1—GENERAL AND PHYSICAL CHEMISTRY

106. **Magnetism of compounds.** K. Kido. *Gakujitu Kyôhô*, **13**, 422—425 (1938).—From the magnetic susceptibilities of inorganic compds., chief alkali and alkaline earth salts, the magnetic susceptibilities of the ions forming these salts were measured and it was ascertained that the magnetic susceptibility of the heteropolar molecule is given as the algebraic sum of those of the ions forming it. This is applicable even to organic compds. or other homopolar compds. and the results obtained agree with the observed value better than those calcd. by Pascal's law, i.e. those additively calcd. from the magnetic susceptibilities of the atoms forming the molecule. J.C.I.

107. **Liquids of standard viscosity.** S. Fujita. *J. Soc. Chem. Ind. Japan*, **41**, 587—590 (1938).—The author carefully calibrated the Höpler viscometer by employing water alone as the standard, and found that consts. of the falling balls of the Höpler viscometer were considerably different from the values given by the maker of the viscometer. By the measurement of the viscosity of standard liquids (No. 3A & No. 611) obtained from the United States Bureau of Standard, it was shown that it checked very well. The viscosities of two other hydrocarbon oils used for other purposes were measured at different temps. Author.

108. **The measurement of solubilities of thallous bromide and iodide by the polarographic method.** Y. Terui. *Bull. Inst. Phys. Chem. Research*, **17**, 595—601 (1938).—The satd. solns. of thallous bromide in aqu. solns. of KBr, whose concns. were 0,0005 to 0,05 mol per liter were electrolysed polarographically, and the concns. of thallium detd. In the same way the solubilities of thallous iodide in aqueous solns. of KI (concns. 0,0001—0,001 mol per liter) were measured. From the solubility volues the solubility products were calcd.:

$$[Tl^{\cdot}]\,[Br']=3.8\times10^{-6}$$
$$[Tl^{\cdot}]\,[I']=5.5\times10^{-8}.$$ Author.

109. **The estimation of lead and cadmium contained in metallic zinc by the polarographic method.** Y. Terui. *Bull. Inst. Phys. Chem. Research*, **17**, 644—648 (1938).—Lead and cadmium, the common impurities in commercial metallic zinc, were estimated simultaneously by the polarographic method. Five specimens of commercial metallic zinc were exaind. About 8 g of each sample were dissolved completely in 70 cc of 5 N HCl with the aid of a few drops of concd. HNO_3. By evaporation the volume of the soln. was made 50 cc and electrolysed polarographically. From the heights of the waves in the polarogram the concns. of lead and cadmium were detd. and percentages of both metals in the sample calcd.

Author.

110. **Twin lamellae of boric acid, BO_3H_3.** H. Tazaki. *J. Sci. Hiroshima Univ.*, A, **9**, 21—27 (1939).— Thin twin lamellae, parallel to the c-face, are frequently exhibited by boric acid crystals obtained by ordinary recrystalliza-

tion from aqueous soln. In this investigation these twin lamellae were examd. by treating the Laue-photographs with the crystallographic globe. Three different types of twinning were observed. The composition planes were all the plane [c01] and the twinning-axes were the crystallographic axes [230], [010] and [4$\bar{1}$0]. No lamella of boric acid, parallel to the c-face, was observed which was built up of two or more individuals having an irregular arrangement, instead of twinning. Author.

111. **Studies on nickel catalysts for the conversion of water gas.** S. Tsutsumi. *J. Chem. Soc. Japan*, **60**, 311—313 (1939).—The amt. of potassium nitrate required to depress the side reaction almost to nil to form methane at the conversion of water gas at 400°C was 1.5–2.0 g uniformly for Ni, Ni–10% Al_2O_3, Ni–5.0% Al_2O_3 and Ni–2.5% Al_2O_3 catalysts, and 0.2 g and more for a Ni–10% CuO catalyst, each of which contains 6 g of nickel. The rate of the formation of methane at 400°C with a Ni–10% MgO catalyst decreased gradually with an increase from 0 g to 2 g in the amt. of potassium nitrate added to 6 g of nickel, but was not depressed to nil, in spite of the fairly small rate of the formation of methane with a similar catalyst contg. no potassium nitrate. Potassium carbonate was found not to be so effective for the depression of the formation of methane at the conversion of water gas. Author.

112. **A new simple theory of valency.** R. Tsuchida. *J. Chem. Soc. Japan*, **60**, 245—256 (1939).—By assuming that molecules and radical ions are built up by co-ordinating molecules, ions and electrons around central cations, configurations of all the simple compds. as well as the complex ones could be readily found. Some of the theoretical results are as follows: $BeO_2^{=}$, BO_2^{-}, CO_2, $[Ag(CN)_2]^{-}$, $Zn(C_2H_5)_2$, CH_3MgI, etc., linear; H_2O, V-shaped (109°); NO_2^{-}, NO_2, SO_2, etc., V-shaped (120°); BCl_3, $CO_3^{=}$, NO_3^{-}, SO_3, $C(NH_2)_3$, $[Ni(CN)_3]^{-}$, etc., plane-triangular; $SO_3^{=}$, ClO_3^{-}, NH_3, etc., pyramidal; dimethylglyoximonickel, $[PtCl_4]^{=}$, $[Pt(NH_3)_4]^{++}$, $[CoCl_4]^{-}$, etc., plane-tetragonal; PO_4^{3-}, $SO_4^{=}$, ClO_4^{-}, NH_4^{+}, $CrO_4^{=}$, $MnO_4^{=}$, MnO_4^{-}, $Ni(CO)_4$, $SnBr_4$, $Pb(C_2H_5)_4$, $[Cu(CN)_4]^{3-}$, $[Zn(NH_3)_4]^{++}$, etc., tetrahedral; SF_6, IO_6^{5-}, $[PtCl_6]^{-}$, $[Fe(CN)_6]^{3-}$, $[NbF_5O]^{-}$, $[Cr(H_2O)_6]^{3+}$, etc., octahedral; OsF_8, $[W(CN)_8]^{-}$, etc., cubic. The results coincide fairly well with exptl. data. A new definition of valency has been proposed; viz., the valency of an element in a given compd. is equal to the number of electrons which the atom of the element in question makes use of in order to form the compd. The structure of benzene, graphite and free triarylmethyl radicals may be explained without assuming the resonance effect. Author.

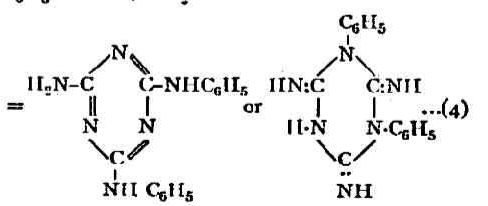
113. **Studies on some derivatives of calcium cyanamide. (VI & VII) Formation of guanidine and its derivatives from dicyandiamide by reaction between dicyandiamide and amine salts. (A) Mechanism of reactions between dicyandiamide and ammonium salts.** K. Sugino. *J. Chem. Soc. Japan*, **60**, 267—275, 351—365 (1939), and *Bull. Tokyo Univ. Eng.*, 8, 99—131 (1939).—Dicyandiamide is converted by its reaction with ammonium salts into guanidine salts, $C_2H_4N_4+2NH_3\cdot HX=2CH_5N_3\cdot HX$. The mechanism of this reaction detd. by the author was as follows: 1) Dicyandiamide is converted primarily into biguanide monosalt by the addition of 1 mol of ammonium salt. $NH_2\cdot C(NH)\cdot NH\cdot CN+NH_3\cdot HX=(NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HX$.....(1). 2) Biguanide monosalt is next converted into 1 mol of guanidine salt and 1 mol of cyanamide or 1/2 mol of dicyandiamide by thermal decompn. $(NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HX=(NH_2\cdot C(NH)\cdot NH_2)HX+NH_2\cdot CN$.....(2). $(NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HX=(NH_2\cdot C(NH)\cdot NH_2)HX+1/2(NH_2\cdot C(NH)\cdot NH\cdot CN)$.....(2'). 3) The cyanamide or dicyandiamide formed in nascent state reacts immediately with ammonium salt and 1 mol of guanidine salt or 1/2 mol of biguanide monosalt is formed successively. $NH_2\cdot CN+NH_3\cdot HX=(NH_2\cdot C(NH)\cdot NH_2)HX$.....(3). $1/2(NH_2\cdot C(NH)\cdot NH\cdot CN)+1/2\ NH_3\cdot HX=1/2(NH_2\cdot$

$C(NH)\cdot NH\cdot C(NH)\cdot NH_2)\,HX$ .....(3′). The biguanide salt formed according to formula (3′) is again decompd. to guanidine salt and dicyandiamide (formula (2′)). Reactions (2) and (3) take place at higher temps. (at least above 160°C), whereas reactions (2′) and (3′) do at lower temps. Author.

114. **On the hydrolysis of zinc sulphate and the formation of basic sulphate.** H. Hagisawa. *Bull. Inst. Phys. Chem. Research*, 18, 368—381 (1939).—The *pH* values of zinc sulphate solns. were detd. at 25° by means of the glass electrode. Different values were obtained according to the method of purification of zinc sulphate crystals. Practically concordant values were found with the crystals which were obtained by cooling a satd. soln. at 70° to 0°, and with those obtained by pptg. with alcohol from a satd. soln. at the ordinary temp. both processes being carried out under the satn. with CO_2. Using the former crystals the *pH* values of solns. of various concns. were measured, and the result may be represented by the following eq. $pH=5{\cdot}340+0{\cdot}441\,7\log V$ (Dilution $V=10$ 1 000). Based on these results, the hydrolysis of zinc sulphate is discussed, and the following eq. is considered most adequate to the exptl. results: $Zn^{\cdot\cdot}+H_2O\rightleftarrows ZnOH^{\cdot}+H^{\cdot}$. The hydrolysis const. was calcd. as follows: $K_h=(a_{ZnOH}\times a_{H})/a_{Zn}=6{\cdot}5\times10^{-11}$ (25°). The potentiometric titration of zinc sulphate soln. with NaOH was performed at 25° by means of the glass electrode. When the concn. of $ZnSO_4$ is greater than 0·007 4 mol/*l*, the ppte. has the composition $ZnSO_4{\cdot}3Zn(OH)_2$ which was ascertained by the analysis of the ppte. When the concn. is very small (0.000 495 5 mol/*l*), the ppte. is $Zn(OH)_2$ and its solubility product was found to be $3{\cdot}4\times10^{-16}$. Large differences in the solubility product of $Zn(OH)_2$, according to the writer's opinion, may be due to the different state of aggregation of the ppte. when produced from solns. by the addition of alkali in various conditions of expts. Author.

115. **Studies on some derivatives of calcium cyanamide (VIII). Formation of guanidine and its derivatives from dicyandiamide by reactions between dicyandiamide and amine salts. (B) Mechanism of reaction between dicyandiamide and aniline-HCl.** K. Sugino. *J. Chem. Soc. Japan*, 60, 411—423 (1939), and *Bull. Tokyo Univ. Eng.*, 8, 151—170 (1939).—In the previous paper (part 6 & 7), the mechanism of the reaction between dicyandiamide and ammonium salt is detd. This report is intended to generalise this mechanism by the reaction between dicyandiamide and aniline-HCl. In this case, it is well known that the phenylbiguanide-HCl (the primary reaction product) is formed quantitatively. In fused states, the thermal decompn. of phenylbiguanide-HCl and the reaction between phenylbiguanide-HCl and aniline-HCl or ammonium chloride were then studied successively. The reactions between phenylcyanamide or cyanamide and amine salts (in fused state) and mutual reactions of cyanamides are also studied in order to discover the mechanisms, which are now believed to be as follows:—

$NH_2\cdot C(NH)\cdot NH\cdot CN+C_6H_5NH_2\cdot HCl$
$=(NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NHC_6H_5)HCl$ .....(1)
$(NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NHC_6H_5)$
$HCl\swarrow{}^{(NH_2\cdot C(NH)\cdot NH_2)HCl+C_6H_5NH\cdot CN}$ ...(2)
$\searrow_{(C_6H_5NH\cdot C(NH)\cdot NH_2)HCl+NH_2\cdot CN}$ ...(2′)
$C_6H_5NH\cdot CN+C_6H_5NH_2\cdot HCl$
$=(C_6H_5NH\cdot C(NH)\cdot NHC_6H_5)HCl$ .....(3)
$C_6H_5NH\cdot CN+NH_3\cdot HCl$
$=(C_6H_5NH\cdot C(NH)\cdot NH_2)HCl$ .....(3)
$NH_2\cdot CN+C_6H_5NH_2\cdot HCl$
$=(C_6H_5NH\cdot C(NH)\cdot NH_2)HCl$ .....(3′)
$NH_2\cdot CN+NH_3\cdot HCl$
$=(NH_2\cdot C(NH)\cdot NH_2)HCl$ .....(3″)
$2C_6H_5NH\cdot CN+NH_2\cdot CN$



...(4)

In the case of phenylbiguanide salt (an unsymmetrical biguanide), two reactions take place in the thermal decompn. It is converted

The Review of Physical Chemistry of Japan Vol. 13f No. 3 (1939)

to (a) guanidine salt and phenylcyanamide (formula (2)) and (b) phenylguanidine salt and cyanamide (formula (2′)). The cyanamides formed in a nascent state react immediately with amine salts and the corresponding salts of guanidines are formed (formula (3), (3′)). A part of cyanamides react together and the phenyl derivatives of melamine (for example: diphenylmelamine (or diphenylisomelamine)) are produced as by-product (formula (4)). Author.

116. **On the longitudinal magneto-resistance effect at various temperatures in iron-nickel alloys.** Y. Sirakawa. *Sci. Repts. Tôhoku Imp. Univ.*, 27, 485—531 (1939).—The change in electric resistance of alloys of the system iron-nickel at various temps. ranging from −195° to 850° was measured up to 1600 oersteds in longitudinal magnetic fields. The specimen used was a fine wire, 0.22~0.61 mm in diameter and 2.6~7.0 cm in length. The change in resistance of the alloys of face-centered cubic solid soln. in nickel side is very much larger than that of the alloys of body-centered cubic solid soln. in iron side, especially at low temps. The magneto-resistance — concn. isothermal curves consist of two portions, separated from each other at a concn. a slightly more than 30% of nickel, and the curves in each portion are concave towards the concn. axis. Author.

117. **On the longitudinal magneto-resistance effect at various temperatures in iron-cobalt alloys.** Y. Sirakawa. *Sci. Repts. Tôhoku Imp. Univ.*, 27, 532—560 (1939).—The change in electric resistance of alloys of the system iron-cobalt at various temps. ranging from −195° to 1150° was measured up to 1600 oersteds in longitudinal magnetic fields. The specimen used was a fine wire, 0.20~0.61 mm in diameter and 3.9~7.1 cm in length. The change in resistance of the alloys of face-centered cubic γ-solid soln. is very much larger than that of the alloys of body-centered cubic α-solid soln. in iron side and of hexagonal close-packed h solid soln. in cobalt side, especially at low temps. The magneto-resistance — concn. isothermal curves consist of three portions, that is, α-, γ- and h-solid soln.; the curves of α-solid soln. alloys are all concave towards the concn. axis. Author.

118. **Measurements of luminous efficiency of sulphide phosphors.** T. Azuma and T. Nagasawa. *Mazda Kenkyu Jiho*, 14, 45—47 (1939).—Certain modifications were introduced to the Guild flicker photometer with the purpose to use also as heterochromatic brightness-meter, and as an example of its application, the luminescent brightness of a film of a sulphide phosphor excited by the monochromatic source of 365 mμ is measured. With examples it is shown that the luminescent efficiency of that phosphor will be computed from the above data combining with the measurements of the absorption of u.v. radiation by the film and the distribution of its luminescence by modifying the distribution-meter; and the quantum efficiency of that phosphor will be also computed when the spectral energy distribution of the luminescence is obtained by photographic spectrophotometry. Authors.

119. **The dielectric constants of solid acetylene tetrachloride, ethylene dichloride, and ethylene chlorobromide.** M. Kubo. *Sci. Papers Inst. Phys. Chem. Research*, 35, 462—465 (1939).—The dielectric consts. of solid acetylene tetrachloride, ethylene dichloride, and ethylene chlorobromide were measured. For acetylene tetrachloride, contributron of dipole to the dielectric const. is not observable in the solid state. It may be concluded that, even though the stable molecular form be polar, crystal force fixes the molecule in the lattice with such rigidity that orientation of dipoles is prohibited in the applied external field, the dielectric const. being nearly of the same magnitude as for substances consisting of nonpolar molecules. Discontinuity in the dielectric const. could not be detected for ethylene dichloride even at the temp. at which the study of cooling

The Review of Physical Chemistry of Japan Vol. 13f No. 3 (1939)

curve has revealed the existence of a transition point. Perhaps above the transition point one-dimensional rotation of molecules in non-polar trans-form is taking place affecting the dielectric const. in a negligible way. The behaviour of ethylene chlorobromide is similar to that of ethylene dichloride, there being no dielectric evidence of a transition in the solid state. The mean molecular state in solid coincides with the trans-position, in which the molecule is practically non-polar owing to the nearly same values of the two bond moments, those of C-Cl and C-Br, oppositely directed to each other. Therefore even if the molecule rotates as a whole, the dipole contribution will not be observable in the dielectric const. of the solid. Authors.

120. **The molecular configuration of diphenyl ether as revealed by dipole moment data.** K. Higasi and S. Uyeo. *Bull. Chem. Soc. Japan*, **14**, 87—101 (1939).—The dipole moments of 2.2′-dinitro-, 2.2′-diiodo-, and 2.2′ dimethyl-diphenyl ethers were measured in benzene and hexane solns. at 27° and 50°. Four isomers of dimethyl-diphenyl ethers were also studied in benzene soln. at 30°. The results obtained for them lead to the conclusion that each benzene ring is perpendicular to the other ring in the molecules considered. Authors.

121. **Raman spectra and the transition point of diiodoethane.** Y. Morino and H. Shimidu. *J. Chem. Soc. Japan*, **60**, 219—221 (1939).—Raman spectra of 1.2-diiodoethane are measured in solid state as well as in solns. The Raman frequencies in the solid are 134(7), 583(10), 1043(5), 1191(6), and 2955(5). It is concluded that the molecular form of $C_2H_4I_2$ is the trans-form in solid state. The rotational transition point is also detd. to be +26.7°C. from thermal measurement. Authors.

122. **On the transition points of 1.2-dihalogenoethane.** Y. Morino. *J. Chem. Soc. Japan*, **60**, 222—226 (1939)—The transition points of 1, 2-dihalogenoethane are detd. by thermal measurement. The results are −65°C for $C_2H_4Cl_2$, −24.7°C for $C_2H_4Br_2$, and +26.7°C for $C_2H_4I_2$. These transitions are attributed to the onset of one-dimensional rotation of the molecules in the crystal lattice, the axis being X-C-C-X. Author.

123. **Selective solvation of LiCl in mixed solvents. Experimental part.** Y. Kobayashi, K. Taka and M. Miura. *J. Sci. Hiroshima Univ.*, **A**, **9**, 33—50 (1939).—Density at 25°C has been detd. for mixts. of urea (0∼36%)-water, urethan (0∼39%)-water and for solns. of LiCl (m=0.5) in these 2 mixts., from which the apparent molal volumes (ϕ_2) of LiCl in the mixed solvents have been calcd. While the decrease of ϕ_2 in EtOH-water mixt. (found in Butler's density data) is but slight up to an alcohol content about 40%, ϕ_2 in urea-water mixt. increases rapidly with the content of urea. The curve of ϕ_2 in urethan-water mixt. first goes down very slowly and then begins to rise and passes the value in the pure water; thus the curve presents an S-shape. **Theoretical part.** Y. Kobayashi, *ibid.*, **9**, 51—66 (1939).—The change in the apparent molal volume of LiCl in EtOH-water, urea-water and urethan-water mixts. is discussed having recourse to various phys. properties, such as compressibility, dielectric const., etc., of the mixed solvents. A conclusion is drawn about the structure of solvate sheath around Li^+-ion in these solvents. Authors.

124. **Absorption bands of metallic complexes. V. Complex salts of transition elements lacking the first band.** S. Kashimoto and R. Tsuchida. *J. Chem. Soc. Japan*, **60**, 347—350 (1939).—The complex salt has generally two or more absorption bands, the first of which has been attributed to electron transition in the transition shell of the central ion. The criterion for the existence of the first band, therefore, is that the central ion must be of a transition element and, moreover, its transition shell must be unsatd. The theory has been corroborated expti. by showing that the first band was not observed

for $K[Ag(CN)]$, $K_3[Cu(CN)_4]$, $K_2[Zn(CN)_4]$ and K_2CrO_4. An app. has been devised for prepg. solns. in air-tight space in order to avoid undesirable effect of atm. oxygen.
Authors.

125. **Extended co-ordination theory. I. Configuration of simple compounds of typical elements.** R. Tsuchida. *Bull. Chem. Soc. Japan*, 14, 101—106 (1939).—All the chemical linkages may be explained in terms of co-ordinate covalence. By assuming that molecules and radical ions are built up by co-ordinating molecules, ions and electrons as ligands around central cations, the configuration of all the simple as well as complex compounds could be readily found. For example, three neg. hydrogen ions and a pair of electrons are assumed to co-ordinate around a quinquevalent nitrogen cation. Then the four ligands are combined tetrahedrally by the general rule of symmetrical co-ordination, and the resulting configuration of NH_3 is a pyramid containing an angle of 109° between two N-H bonds, the actual value being 106°. When two neg. hydrogen ions and two pairs of electrons are co-ordinated around a sexavalent oxygen kernel, the resulting water molecule is V-shaped, the angle between two H-O bonds being 109° for the exptl. result of 105°. By co-ordinating three bivalent oxygen anions around a sexavalent sulphur cation, we have the planar molecule SO_3, whereas a pyramidal configuration is obtained for SO_3^{--} ion, in which four ligands, i. e., three bivalent oxygen ions and a pair of electrons, are concerned. Author.

126. **On the thermoelectric properties of the superlattice alloy $AuCu_3$.** Y. Takagi and T. Satô. *Proc. Phys.-Math. Soc. Japan*, III, 21, 251—258 (1939).—The change of thermoelectric power of the superlattice alloy $AuCu_3$ was measured in the course of the order-disorder transformation. The change thus found is very conspicuous, and in its general tendency it bears very much resemblance to the change of resistivity in the course of this transformation. Some theoretical considerations were made adopting the nearly free electron models. Authors.

127. **On the determination of the viscosity by the torsional vibration.** I. T. Okaya and M. Hasegawa. *Proc. Phys.-Math. Soc. Japan*, III, 21, 347—353 (1939).—The authors have shown that, for the detn. of viscosity of a liquid, one may make use of the torsional vibration of a hollow cylinder filled with the liquid whose viscosity is to be detd. and suspended axially at the center of its upper base by means of an elastic string. As the vibration is of the damped one, we can measure the logarithmic decrement and thence deduce the coeff. of viscosity according to the formulae which one of the authors had obtained (*ibid.*, III, 16, 268 (1936)). By this method, the authors have measured the coeff. of viscosity of a kind of gasolene at various temps. (17°~38°C) and found that, even for the mixt. of liquids whose constituents possess the different temp. of evaporation, as the case of gasolene, the Andrade formula $\mu = Ae^{B/K}$ (μ: viscosity, K: absolute temp. of gasolene, A, B: certain consts.) is also valid for any temp. lower than the lowest temp. of evaporation which some of the constituents shows. Authors.

128. **The re-measurement of the concentration of heavy hydrogen in ordinary water.** T. Morita and T. Titani. *Bull. Chem. Soc. Japan*, 13, 419-426 (1938).—In electrolysing ordinary water, oxygen having the same isotope composition as ordinary water was prepd. by repeated use of the same electrolyte soln. With light hydrogen it was turned into light water, whose density was compared with the original ordinary water. Thus the concn. of heavy hydrogen in ordinary water was calcd. to be $D : H = 1 : 6{,}200 \pm 200$. This value holds good for both the drinking water of Osaka and that of Cambridge, Mass., U. S. A. J. C. L.

129. **The velocity of the exchange reaction of the hydrogen atoms between hexoses and water.** M. Koizumi and T.

The Review of Physical Chemistry of Japan Vol. 13f No. 3 (1939)

Titani. *Bull. Chem. Soc. Japan*, **13**, 427–436 (1938).—In order to exam. the velocity of the exchange reaction of the hydrogen atoms between the OH radical present in organic compds. and water, the following expts. were carried out on grape sugar, fruit sugar, glycerin, glycol, etc. These substances were dissolved in heavy water. The concn. of heavy hydrogen present in the soln. thus made was measured at various intervals. It was found that the velocity of the exchange reaction for all these substances was so large, independent of the nature of each soln., that the reaction ended in 1 min. The distribution coeff. of heavy hydrogen between hexoses and water was found to be $\alpha=1.15$. The practical coeff. is expected to be less than the value.

J. C. L.

130. **The exchange reaction of the oxygen atoms between water and some organic compounds. (Preliminary report).** M. Koizumi and T. Titani. *Bull. Chem. Soc. Japan*, **13**, 463–464 (1938).—Using heavy oxygen, the reaction in question was studied. The results obtained were as follows:

Substance	Exptl. temp.	Time (hr.)	The number*
Glucose	100°	0~3	1
Benzaldehyde	110°	1~2	1
Benzoic acid	130°	1~5	1
Phenol	100°	24~48	<1
Succinic acid	130°	1	2
„	„	2~5	4
Maleic acid	100°	20~45	4
Fumaric acid	100°	3~45	2
Phthalic acid	100°	20	<1
Terephthalic acid	100°	20	<1

(* The number indicates the exchangeable o contained in one molecule.) Concerniug the results, some preliminary considerations are given.

J. C. L.

131. **A new formula of dilution.** T. Yoritaka. *Osaka Igakukai Zasshi*, **37**, 1847–1856 (1938).—A new simple device is proposed, which enables one to make any desired diluted soln. of x% from a given concd. one of p%. Representing the sp. gr. of the latter by d, the volume cc of the given soln. required for the prepn. of 100 g. soln. of x% is Gx where G=100/pd and that of water to be added is P(p−x) where P=100/p. Both G and P being known, it is simple for one to make a table of required quantities of the given soln. and water for various dilutions. Weighing is not required at all Author.

132. **The exchange reaction of the oxygen atoms between some inorganic negative ions and water (A preliminary report).** T. Titani and K. Gotô. *Bull. Chem. Soc. Japan*, **13**, 667–668 (1938).—When heavy water containing heavy oxygen, in which such a neutral salt as K_2SO_4 or $NaClO_3$ has been dissolved, is heated to 80° or 100°, no exchange reaction of the oxygen atoms is observed. In the case of such an acid salt as KH_2AsS_4 or KH_2PO_4, an exchange reaction takes place at room temp.~100°: the oxygen atoms present in an acid salt is completely replaced by those of water. Even when a small amt. of $KHSO_4$ or HCl is added to the above-mentioned neutral salt, an exchange reaction takes place. It is probable that this catalytic action of H is caused by the formation of the free acid molecules produced by H^+ and by the exchange reaction between this H and the water molecules.

J. C. L.

133. **The isotopic exchange reaction of gaseous oxygen. III. The exchange reaction between oxygen and water vapour by copper oxide.** T. Morita and T. Titani. *Bull. Chem. Soc. Japan*, **13**, 656–667 (1938).—The exchange reaction in question with copper oxide used as the catalyst was studied. The exchange reaction took place slightly at temp. below 650°C and remarkably at 650–750°C and completely above 750°C. In order to clarify the catalytic mechanism of this reaction the isotopic exchange reaction of oxygen between oxygen and copper oxide and also between water vapour and copper oxide was examd.: in the

former case no exchange reaction took place even at 900°C; in the latter case the exchange reaction took place at the same temp. and the temp. change of the exchanged amt. is similar to that of the reaction between oxygen and water vapour. Judging from this and the facts that copper oxide does not adsorb oxygen but does water vapour so well and also that the oxide tends to be reduced at high temps., it is concluded that the exchange reaction in question is caused by the action of the intermediate compd. produced in the reaction between water vapour and copper oxide and the rate of reaction depends on its decomposition. J. C. I.

134. **Studies on the oiliness of liquids. VI. Measurements of the kinetic friction coefficients by the method of sliding velocity.** T. Sasaki. *Bull. Chem. Soc. Japan*, **13**, 134–141 (1938).—Measurements of the kinetic friction coeff. were made to study the oiliness of liquids. The method consists of the observation of the sliding velocity of a slider on an inclined surface lubricated with the liquid to be tested. Special app. was constructed to measure the sliding velocity. It is confirmed that the kinetic friction coeff. is generally independent of the velocity over the range of the expt. (up to about 100 cm./sec.), and the following equation holds.

$$\tan\theta-\frac{(\sqrt{2S_2}-\sqrt{2S_1})^2}{g}v^2\sec\theta=\mu k$$

where v is the mean velocity of the slide on the surface of the inclination θ. The above equation lacks the viscosity term, so the conditions of the boundary lubrication are considered to be satisfied. The kinetic friction coeffs. of glycerin, aliphatic hydro-carbons, aliphatic alcohols, acetic acid, and water were measured. Author.

135. **The detection of ultra-short waves by an ionized gas tube.** Y. Miyamura. *Bull. Electrotech. Lab.*, **3**, 221–222 (1939).—Various papers have already dealt with the high-frequency characteristics of ionized gas tubes and their application to the modulation of micro-waves and ultra-short waves. The author thought of a new method of using such a tube as a detector. This method consists in first causing a 100-volt neon lamp (to be called here an ionized detector), having a spiral electrode, to discharge by connecting to it a suitable series resistance and a voltage source, and then connecting a suitable parallel-line feeder to the terminals of the detector. If the ultra-short wave input through this line to the ionized detector is varied, the discharging current will also vary. This variation is nearly linear, and hence it is seen that the tube may be used for detection. The actual measurements were conducted at 148 megacycles. A receiver using this detector was built, and waves were received from an oscillator modulated at 1000 cycles. The results were fairly good. The question of how feasible the ionized detector is, cannot be clearly answered until further research is performed. Since the detector response will vary with the structure of the electrode, its material, the kind of gas enclosed in the tube, and the press., investigations must be carried out to det. how these factors should be chosen to give optimum characteristic. Besides the spiral electrode, tests were also conducted on parallel plane electrodes and a small type of detector tube during the expt., but it was found that the tube containing the spiral electrode showed the best characteristic. It is also conceivable that there is a relationship between the frequency of the applied wave and the gas press. for optimum detector response. This detector is believed to be also effective in the micro-wave region. Author.

136. **A method for observing the distribution of lines of magnetic force through the Faraday effect: the magneto-optical method.** T. Takei and Y. Hosino. *J. Electrochem. Assoc. Japan*, **7**, 121–125 (1939).—A magneto-optical device for observing the Faraday effect, involving the "Dichrom" polarizing plate combined with the satd. water soln. of K_2HgI_4 and arranged

with a suitable system, is described. The device permits the photographical or eye-observation of the distribution of lines of magnetic force on a considerably wide area. This being characterized by its extremly decreased thickness in comparison with the customary exptl. app. for measuring the Faraday effect, an observation of the magnetic field confined to the narrow space is also possible. The general consideration on the construction of this magneto-optical device and the photographing method are given, showing the magneto-optical photographs obtained by the present device. Authors.

137. **Studies on the oiliness of liquids. V. Lubricants consisting of two or three chemical compounds.** H. Akamatu. *Bull. Chem. Soc. Japan*, **13**, 127–133 (1938).—The static boundary frictions were measured when some binary or ternary mixts. were placed on the glass surfaces. The results suggest that: (i) the friction is governed by the surfaces with adsorbed layer of lubricant, and (ii) the power of reducing friction depends upon the individual molecular constitution of the molecules which are adsorbed preferentially by the friction surface, rather than the stability of the film. Selective adsorption by the glass surface was investigated, and some examples are reported. Authr.

138. **The investigation of thin films of cellulose derivatives by electron diffraction (A preliminary report).** J. Kakinoki. *Proc. Phys.-Math. Soc. Japan*, **III**, **21**, 66–74 (1939).—To the analysis of the electron diffraction patterns produced with the films of collodion and nitro-cellulose is applied the method of analysis for the gas diffraction, and it is found that the patterns are produced by complex arrangement of molecular chains. J.C.L.

139. **A molecular compound of $FeCl_3$ extracted by ether from hydrochloric acid solutions.** S. Katô and R. Ishii. *Sci. Papers Inst. Phys. Chem. Research*, **36**, 82–96 (1939).—By chem. method as well as the observation of absorption spectra, the following conclusions have been reached in regard to the conditions, under which ferric chloride is extracted from its hydrochloric acid soln. by ether in a form of molecular compd. (1) It is surmised that undissociated molecules of $FeCl_3$ exist in its soln. in hydrochloric acid of $N/40$ or so, and that the number of such molecules increases with the increase of concn. of acid. (2) Solns. of $FeCl_3$ in hydrochloric acid of about 3.5 N give an effect of molecular field to the $FeCl_3$, and the effect increases with the increase of concn. of HCl, its max. being reached at about $7N$. At concns. higher than $7N$ the effect decreases. (3) Thus $7N$ is regarded as optimum concn. for the extraction of $FeCl_3$ by ether. (4) Absorption spectra given by the ether extract of $FeCl_3$ are very similar to those given by a soln. of $FeCl_3$ in concd. (about $12N$) hydrochloric acid. This fact suggests that the molecular compd. extracted by ether contains at least a molecular group indicated by $FeCl_3 \cdot HCl \cdot 3H_2O$. Since the molecules of HCl and $FeCl_3$ must be arranged in such a way that their dipole moments are mutually reduced, a diagram may be given which shows the probable structure. Three molecules of H_2O will be arranged one by one on the three planes detd. by $FeCl^1Cl^2$, $FeCl^2Cl^3$, and $FeCl^3Cl^1$ resp., two hydrogen atoms of H_2O being situated near the two Cl atoms, and one oxygen atom near the Fe atom. (5) Investigation by chem. method has shown that the constitution of the compd. in question is represented by the formula, $2[FeCl_3 \cdot HCl] + 9H_2O + 15(C_2H_5)_2O$. In the method, the gradual decrease in the weight of ether extract by slow evaporation, and the compn. of residual solns. at various steps of evaporation have been detd. Authors.

140. **On the thermal conductivity of liquid.** I. Osida. *Proc. Phys.-Math Soc. Japan*, **III**, **21**, 353–356 (1939).—Making the assumption that a molecule in a liquid has 6 degrees of freedom corresponding to its trans-

The Review of Physical Chemistry of Japan Vol. 13f No. 3 (1939)

lational and rotational motion and that an energy of kT/2 (k is Boltzmann's const. and T the absolute temp. of the molecule) is distributed to each freedom, and also that the energy is transferred by the collision between the molecules when there is a temp. difference in the liquid, the author calcd. the conductivity K: $K=3.1\times10^{-3}(Tm^{1/2})/(M^{1/4}V^{2/3})$ cal. $cm.^{-2}$ $deg.^{-1}$ where Tm is the absolute temp. of M. P., M the molecular weight and V the molecular volume. Comparing the results with the exptl. values, the calcn. is considered to be satisfactory if the simplicity of the theory is taken into account. J.C.L.

141. **Arrangement of the micro-crystals of silver bromide electro-deposited on the anode silver plate.** S. Shimadzu. *Gakujitu Kyoho*, **14**, 210–213 (1939).—X-ray studies on substances electro-deposited on the electrode in the soln. of an electrolyte have been carried out mainly on the micro-crystals of metals deposited on the cathode. In the present expt. the author examd. the micro-crystals of silver bromide electro-deprsited on the anode silver plate in a water soln. potassium bromide. It was found that the arrangement of the micro-crystals is largely affected by the existence of acid or alkali in the soln. Author.

142. **Extended co-ordination theory of valency. (II) Configuration of carbon compounds.** R. Tsuchida. This Journal **13**, 31–41 (1939).

143. **Extended co-ordination theory of valency. (III) Valence bonds in carbon compounds.** R. Tsuchida and M. Kobayashi. This Journal, **13**, 61–73 (1939).

2—ATOMIC STRUCTURE, RADIOCHEMISTRY AND PHOTOCHEMISTRY

144. **The absorption spectrum of coloured solutions of inorganic salts. II.** K. Harai. *J. Chem. Soc. Japan*, **59**, 899—901 (1938).—With respect to the alcoholic solns. of chlorides of rare earth metals, such as Pr, Nd, Sm and Er, the absorption spectra at −80° were measured in the range between about 9000 Å and 3300 Å. Comparing the results obtained with those at room temp, it was found that there was no splitting in the absorption band of Pr, but many fine splittings in those of Nd, Sm and Er. J.C.L.

145. **High terms of Paschen series in hydrogen and deuterium.** H. Nagaoka and T. Mishima. *Proc. Imp. Acad.*, **14**, 53—56 (1938).—The Paschen series of hydrogen and heavy hydrogen were studied with respect to the luminosity curves of high terms, such as m=23∼27 though with some doubt about peaks higher than 24. The influences of the rays due to such impurities as oxygen and the second order rays of hydrogen, difficulties in detecting these influences and the advantages and disadvantages of polar or non-polar electric discharge are discussed and compared with the results obtained by astronomical observations. J.C.L.

146. **The exchange reaction between oxygen and the water vapour or carbonic anhydride in the presence of platinum.** T. Morita and T. Titani. *Bull. Chem. Soc. Japan*, **13**, 357—370 (1938).—CO_2 and the water vapour, being mixed with electrolytic oxygen obtained from the ordinary water, were passed over platinum asbestos or a platinum wire at various temps., and the exchange reaction between the hydrogen isotopes were examd. When platinum asbestos was used as a catalyst, the amt. of the ex-exchange is very small below 400°C, and suddenly increases at 400°—500°C, until it reaches a max. above 500°C. Both the water

The Review of Physical Chemistry of Japan Vol. 13f No. 3 (1939)

vapour and carbonic anhydride make the exchange of almost the same degree at the same temp. In the case of a platinum wire used as a catalyst, the amt. of the reaction is far smaller than in the case of platinum asbestos, which may be ascribed to the size of the surface area. The amt. of the exchange reaction in the presence of platinum asbestos has no relation to the mixing ratio of the water vapour to oxygen over a wide range. From these facts and the fact that the min. temp. (about 400°C) at which the exchange reaction is observed is the same as that at which the secondary activated adsorption of oxygen by platinum starts, it was concluded that the secondary activated adsorption by platinum plays an important rôle in the exchange reaction between oxygen and the water vapour. J.C.L.

147. **Direct photographic impression of cosmic ray in magnetic field.** T. Takeuchi and T. Sugita. *Proc. Phys.-Math. Soc. Japan*, **III**, **20**, 221—222 (1938) 2 figs.—By means of a Wilson chamber and an electromagnet, curving of cosmic radiation in magnetic field was investigated by several physicists. But for the first time direct photographic impression of curved tracks was successfully obtained by the present authors. The special sensitive plates were placed vertically between the poles of a Nagaoka electromagnet excited by a current of strength 15 A, the polar distance being 4.7 cm. A 6 cm block of lead was placed 10 cm above the poles. After about 1/2 month, they were developed and examd. by a microscope of magnification 300. The authors measured these curved tracks generated by cosmic radiation and found that they corresponded to energy of about 66,000 e-V and less. In addition to the above-mentioned tracks, there were also seen straight ones, capable of penetrating the thick lead block. Authors.

148. **Quantum mechanical resonance and internal rotation.** S. Mizushima and M. Kubo. *Bull. Chem. Soc. Japan*, **13**, 174—181 (1938).—The dielectric consts. of the vapours of methyl acetate, methyl chloroformate, and ethyl chloroformate were measured. The temp. dependence of dipole moments of these compds. was discussed from the standpoint of the effect of single bond-double bond resonance upon the internal rotation. In acids and esters the strong carboxylic resonance imparts the double bond character to the C-O bond of the actual "mesomeric" molecule to such an extent that practically the complete inhibition of the internal motion is realized at ordinary temp. while replacement of hydrogen of H-COOR by chlorine or methoxyl group greatly reduces this double bond character, so that the internal oscillatory rotation of finite amplitude can take place about the C-O bond as axis. Authors.

149. **On the theory of dielectric constant of gases under high pressures.** M. Kubo. *Bull. Chem. Soc. Japan*, **13**, 167—173 (1938).—The repetition and completion of the theory which was already reported. (*Sci. Papers Inst. Phys. Chem. Research*, **27**, 295 (1938)) J.C.L.

150. **Tables of the density and the kinetic viscosity coefficient of the air.** I. Tani and K. Isii. *J. Aeronautical Research Inst. Tôkyô Imp. Univ.*, **165**, 250—255 (1938).—The values of the density and kinetic viscosity coeffs. were calcd. The temp. and press. ranges were −10°~40° and 740~775 mm resp. The density ρ was calcd. according to Tamaru's suggestion, and the viscosity coeff. μ was from the following expression: $\mu = 0.000001821\{1+0.00276(t-15)\}$kg./m². From these values the kinetic viscosity coeff. was obtained. J.C.L.

151. **The influence of kaolin and porcelain clay on the equilibrium of hydrogen ion.** K. Yoshida and K. Hiroki. *Kyoto Furitsu Ika Daigaku*, **12**, 882—888 (1937).—The influence of kaolin and porcelain clay on the equil. of the hydrogen ions of HCl and NaOH was examd. by the method of hydrogen gas electrode. It was found that kaolin made H combine in HCl.

giving no influence on NaOH, while porcelain clay made OH′ combine in NaOH, giving no influence on HCl. To the H combination of kaolin and the OH′ combination of porcelain clay is Freundlich's adsorption isotherm applicable. J.C.L.

152. **The cathode-luminescence of luminescent aluminium oxide.** E. Iwase. *Sci. Papers Inst. Phys. Chem. Research*, **34**, 761—774 (1938).—On several specimens of natural aluminium oxide minerals from Japan as well as from foreign countries, the luminescence under the excitation by cathode rays was examd. Spectrographical studies were made on the cathode-luminescence exhibited by some specimens of Japanese corundum. As the specimens of ruby from North Carolina exceed any other in the brightness of luminescence, so its emissions given by both the cathode rays- and the ultraviolet rays-excitation and its light-transmission were investigated in some details. Some of the emission bands here observed have not yet been recorded by any former investigators. On the luminiferous synthesized materials, Al_2O_3-Bi, Al_2O_3-U, Al_2O_3-Sm, Al_2O_3-Mn, and Al_2O_3-Cr, there were also examd. the influences of the concn. of activation and the calcination temp. upon the colour of cathode-luminescence.

Author.

153. **Image made by X-rays radiated from a crystal surface.** T. Fujiwara and I. Takeshita. *J. Sci. Hiroshima Univ.*, **A**, **8**, 297—302 (1938).—Casting the $K_{\alpha,\beta}$ X-rays of Cu and Zn, which were radiated from the same point of the anticathode, on (100) of NaCl, an interference image made by the reflected rays (a similar one obtained by H. Seeman: *Ann. Phys.* **7**, 633 (1930)) is discussed. J.C.L.

154. **The velocity distribution in an atomic beam and the free path as a function of velocity.** N. Sasaki and M. Fukuda. *Proc. Imp. Acad.*, **14**, 166—169 (1938).—A beam of sodium atoms was sent through an inhomogeneous magnetic field (Stern-Gerlach). The intensity distribution of the velocity spectrum thus produced was measured with a hot tungsten filament. The result shows a deviation from the Maxwell velocity distribution law, slower atoms being deficient. The deviation was explained quantitatively by taking into account the scattering effect due to the sodium vapour cloud formed in front of the furnace slit.

Authors.

155. **The mean free path in gases contained in a vessel.** M. Saito. *J. Inst. Elec. Eng. Japan*, **59**, 231—233 (1939).—The author considered how the mean free path (l) in gases contained in a vessel must be modified as compared with that (F) in the free space and calcd. the mean free path of electron moving to a certain direction in a gas filled vessel, which was geometrically simple, as follows:

(1) between two parallel plates t cm apart,

$$l = F\left[1 + \frac{F}{t}\left(\varepsilon^{-\frac{t}{F}} - 1\right)\right]$$

(2) between two coaxial cylinders,

(a) when moving from the inner (radius R_1) to the outer (radius R_2),

$$l = F\left[1 - \frac{2F(R_2 - F)}{(R_2^2 - R_1^2)} + \frac{2F(R_1 + F)}{(R_2^2 - R_1^2)}\,\varepsilon^{-\frac{R_2 - R_1}{F}}\right]$$

(b) when moving from the outer to the inner,

$$l = F\left[1 - \frac{2F(R_1 + F)}{(R_2^2 - R_1^2)} + \frac{2F(R_2 + F)}{(R_2^2 - R_1^2)}\,\varepsilon^{-\frac{R_2 - R_1}{F}}\right]$$

The above relations are discussed with respect to many curves and the case of concentric spheres also described. Author.

156. **Electron density and interatomic distances in tetragonal pentaerythritol.** I. Nitta and T. Watanabe. *Sci. Papers Inst. Phys. Chem. Research*, **34**, 1669—1680 (1938).—By use of Cu K radiation filtered through Ni and Mo K filtered through ZrO_2 and SrO, oscillation, rotation and powder photographs were taken of pentaerythritol. The photo-

metered intensities of the (*hk*O) and (*h*O*l*) reflections were utilized in the Fourier synthesis of the electron density. Contour maps were prepd. for the projection of the electron density distribution upon (001) and (010). The obtained atomic parameters are: $x=0$, $y=0$, $z=0$ for the central C; $x=0.160$, $y=0.128$, $z=0.100$ for the methylenic C; and $x=0.312$, $y=0.248$, $z=0.002$ for the hydroxyl O atoms. The interatomic bond distances are: C-C, 1.53 A.; C-O, 1.45 A.; O-(H)-O, 2.70 A. The valence angles are: $\angle CH_2$(a), C, CH_2(b), 110°; $\angle CH_2$(a), C, CH_2(c), 109°; $\angle$C, CH_2, O, 108½°, $\angle CH_2$(a), O(a), O(b), 116½°; $\angle CH_2$(a), O(a), O(c), 139½°; this shows nearly a tetrahedral distribution of the methylenic C atoms about the central C. The (001) contour map indicates the deformation of the electronic clouds of O atoms, being presumably direct evidence of hydrogen bridge formation.

Authors.

157. **Photographic spectrophotometry of a continuous spectrum.** T. Azuma. *Mazda Kenkyu Jiho*, **14**, 41—44 (1939).—The photographic spectrophotometry of a continuous spectrum is carried out as follows:— (1) Taking Mazda gas filled optical pyrometer standard lamp lighted at color temp. 2800°K as the standard, its spectrum with intensity marks indicated by a stepped sector or a gradation filter placed before the slit was taken and the micro-photometric curves at each step were superposed taking care to bring the wave lenghths together; while the microphotometric curve of the spectrum of a test lamp (in this case the luminescent spectrum of a sulphide phosphor) taken on the same photographic plate by the same exposure is superposed also on them. (2) The relative spectral intensity curves of the test lamp were calcd. and plotted assuming the intensity at each wave length of the standard lamp as 100, making very small number of calibrations in view of the undulation of the curve. (3) The relative spectral energy distribution of the test lamp expressed in term of normal spectrum is obtained by multiplying the relative intensity at each wave length with the relative spectral energy of black body at 2800°K. Furthermore, there are discussed the important expti. factors:— (1) condition of noting the intensity marks with the Hilger stepped sector, (2) minimizing of the errors caused by the lens chromatisms by the use of diffused silica glass. Author.

158. **The variation of intensities of spectral lines with the direction of observation in the Stark effect.** H. Kubota. *Sci. Papers Inst. Phys. Chem. Research*, **36**, 7—11 (1939).—The relative intensities of spectral lines in the Zeeman or Stark effect are well known both from the expti. and theoretical points of view, when they are observed parallel or perpendicular to the direction of the field (longitudinal- or transversal-effect). However, as to the case when the direction of the observation is not parallel or perpendicular to the field, there has been very little work done. In the present paper, the author proposed an expression for intensity at an arbitrary angle and compared it with the expti. results got by Lo-Surdo tube having a rotating axis.

Author.

159. **On the Stark effect of Ne II spectrum.** Y. Ishida, T. Tamura, and G. Kamijima. *Sci. Papers Inst. Phys. Chem. Research*, **36**, 12—30 (1939).—The spectrum of Ne II was measured first by Merton. Later L. Bloch, E. Bloch, and Dejardin measured more lines extending to ultra-violet; their data were classified by de Bruin and Kichlu on the assumption of LS-coupling. De Bruin continued the analysis further and detd. the absolute term values. Ryde measured the Stark effect of the lines in the violet range and classified some of 5f-configuration. Using the beryllium cathode in Lo Surdo quartz tube, the authors have investigated the Stark effect of this spectrum and found many lines emitted by 3d-nx transitions. The Stark effects of the lines of this category behave similar to that of helium. As to the coupling, the lower configurations seem to obey the normal coupling, while, as n increases, they seem to

follow jj- coupling. Incidentally, the authors have evaluated the absolute term values.

Authors.

160. **Chemical studies by means of molecular beams. VII-VIII. A method of measuring the intensity of potassium atomic beams with an incandescent tungsten surface.** (1—2). K. Kodera. *Bull. Chem. Soc. Japan*, **14**, 114—121, 141—147 (1939).—The surface ionization detector of atomic beams was studied, in which a tungsten ribbon was used in place of a fine filament. Atoms of the beams were condensed on the cold ribbon surface and the deposit was flashed. The evaporated ions by flashing were measured by a ballistic galvanometer. It has been proved that the method is excellent in measuring very attenuated beams of large cross sections. Besides, the behaviour of adsorbed potassium atoms on the tungsten surface was studied and the following results have been obtained:— The ribbon surface is uniform for the ionization of potassium atoms. To evaporate the adsorbed atoms as ions, the ribbon must be heated above 800°C. When the surface concn. of adsorbed atoms is below 0.04 of that of monoatomic layer, the complete ionization is effected by flashing. The ionization efficiency of the adsorbed atoms by flashing as a function of the surface concn. is found to be in good agreement with the calcd. one. The adsorbed atoms begin to migrate on the surface when heated to 500°—700°C. A simple method of detg. the heat of activation of the surface migration is proposed. Author.

161. **On nuclear force.** T. Takeuti. *Gakujitu Kyóhó*, **14**, 217 (1939).—From the author's new idea which was used in calcg. the mass of yukon, a formula of beta-disintegration was obtained. Author.

162. **Photographic demonstration of uranium fission.** T. Takeuti. *Bull. Tokyo Univ. Eng.*, 8, 285—286 (1939).—It was shown by direct photographic impression that uranyl acetate irradiated by γ-rays of radium sulphate was partially converted to an element of less radioactivity and, when bombarded with photo-nuclear neutron, it gave long tracks of emitted particles during the fission.

Author.

163. **The promoter and supporter. V. Change of the active surface of a catalyst by adding a promoter and supporter.** S. Tutumi. *J. Chem. Soc. Japan*, **59**, 893–898 (1938).—In the reaction (I), $CO+H_2 \rightarrow$Benzine and in the hydrogenation of C_6H_6 (II), the effect of the amt. of Cr and kieselguhr added to Ni on the activity of a Ni-Cr catalyst is examd. and compared with the case of a Ni-Al catalyst. (i) In reaction (I) the most favourable ratio of Ni : Cr : kieselguhr is 100 : 7.5 : 50 and the catalytic activity is higher than that when the ratio of Ni : Al_2O_3 : kieselguhr is 100 : 10 : 100. In reaction (II) the result is reverse. (ii) The promoter and supporter serve to keep the reducing metal from melting half at high reduction temps. A relatively large amt. of the supporter is required as compared with that of the promoter. (iii) In reaction (I) the ratio of Ni to the most favourable amt. of kieselguhr is 2 : 1, while in reaction (II) it is 1 : 50. This may be ascribed to the difference between the magnitude of the CO molecule and that of the C_6H_6 and to the difference between the kinds of these two reaction. The reduction of C_6H_6 is a true hydrogenation, while the reduction of CO is a reaction similar to that of a free radical→hydrocarbon. In the latter case, a metal carbide is formed as an intermediate product and then such radicals as $CH\equiv$, $CH_2=$ and CH_3-, are formed.

J.C.I.

164. **Excitation of the Balmer and Paschen series of hydrogen and heavy hydrogen by electrodeless discharge.** H. Nagaoka and T. Misima. *Sci. Papers Inst. Phys. Chem. Research*, **34**, 931–956 (1938).—Through hydrogen or heavy hydrogen kept in a tube 15 cm. in diameter and 100 cm. in length, electrodeless discharge was

The Review of Physical Chemistry of Japan Vol. 13f No. 3 (1939)

passed by means of an excitation coil with a transformer of 3 KW and a condenser of 0.003 μF and the discharge was kept on by passing compressed air through the spark gap to be photographed by means of a Steinheit GII spectroscope. The Balmer series of H and D was photographed as far as n=25, excluding the secondary spectra, and n=37, including what were like the secondary spectra.

J.C.L.

165. **On the continuous emission spectrum accompanying the resonance lines of neon.** T. Takamine, T. Suga, Y. Tanaka and G. Imotani. *Sci. Papers Inst. Phys. Chem. Research*, **35**, 447-454 (1939).—When a condensed discharge is passed through a neon tube contg. a small amt. of nitrogen, a continuous emission spectrum extending to about 50Å is observed on the longer wavelength side of the resonance line of neon λ 744 Å. From the fact that the longer wavelength limit of this emission continuum corresponds energetically to the $^2\Sigma g^+(X')$ level of the molecular nitrogen, it seems likely that the phenomenon shows a certain resonance effect between the excited neon atoms and the nitrogen molecules. Authors.

166. **Vibrational analysis of CCl bands.** T. Horie. *Proc. Phys.-Math. Soc. Japan*, **III**, **21**, 143-148 (1939).—The band-spectrum of CCl in emission has been obtained by means of condensed discharge through continuous flow of carbon tetrachloride vapour. Its vibrational structure has been investigated. The heads are represented approximately by $\nu_h = \begin{Bmatrix}35756.5\\35852.4\end{Bmatrix} + 953.6\,v' - 18.8\,v'^2 - 861.1\,v'' + 3.5\,v''^2$. The transition is probably $^2\Sigma \rightarrow {}^2\Pi$.

Author.

167. **Beta-ray spectrum of ^{24}Na.** S. Kikuchi, Y. Watase, J. Itoh, E. Takeda and S. Yamaguchi. *Proc. Phys.-Math. Soc. Japan*, **III**, **21**, 259-260 (1939).—The beta-ray spectrum of ^{24}Na was investigated with the magnetic spectrometer which was used in the authors' previous expts. investigating the beta-ray spectra of RaE and ^{13}N. ^{24}Na was produced by the Osaka cyclotron by bombarding NaF with deuterons 5.2 Mev in energy. From the energy distribution curve of the spectrum the authors estimated the upper limit to be 1.37±0.03 Mev. This value is considerably lower than the inspection upper limit obtained by Kurie and others and Amaki and Sugimoto from the analysis of Wilson chamber photographs, but it is in agreement with the value obtained by Feather by the absorption method. The number of electrons in high energy region is much smaller than expected from the K.-U. theory. As for K.-U. plot, the authors get for the theoretical upper limit 1.93 Mev, which is 0.56 Mev higher than the inspection upper limit. The general feature of the plot in low energy region is different from the case of ^{13}N. In the latter case, the low energy electrons were relatively more abundant. The Fermi plot can be represented by straight lines having knicks at 1.15 and 0.6 Mev. As the transition from ^{24}Na to ^{24}Mg is considered to be "forbidden," the direct comparison of the result with the theory is at present impossible. However, if we assume that the Fermi distribution function is approximately valid both for allowed and forbidden transition, the ^{24}Mg nucleus should have excited states at 0.22 and 0.8 Mev, and the gamma-rays of energy 0.22, 0.6 and 0.8 Mev are expected.

Authors.

168. **Gamma-rays accompanying the disintegration of ^{24}Na.** S. Kikuchi, Y. Watase, J. Itoh, E. Takeda, and S. Yamaguchi. *Proc. Phys.-Math. Soc. Japan*, **III**, **21**, 260-261 (1939).—Gamma-rays accompanying the disintegration of ^{24}Na was investigated by analysing the secondary electrons emitted from a carbon plate by the magnetic spectrometer. There are two groups of Compton electrons of approximately the same intensity having max. energy edges at 2.74±0.07 and 1.27 ±0.05 Mev and less clearly the third group at 0.6 Mev. The energy of the corresponding gamma-rays are 2.97±0.07, 1.49±0.05 and

about 0.8 Mev resp. The gamma-rays from ^{24}Na was investigated by Richardson and it is reported that they consist of three lines of energies 3.00, 2.04 and 1.01 Mev, whose intensites are in the ratio of about 0.65 : 0.95 : 1.05. The energy value of the hardest component is in good agreement. But as to the other groups, disagreement is far above the expt. error. In connection with the beta-ray spectrum, the analysis of the gamma-rays of energy lower than 1 Mev is important. The present results are not sufficient to decide whether the knicks in Fermi plot are really connected with the excited states of ^{24}Mg nucleus, although the 0.8 Mev gamma-ray is just to be expected from the beta-ray analysis reported in the preceding note. Authors.

169. **Photo-conductance of the dye-sensitized silver bromide and the mechanism of the dye-sensitization. I.** N. Kameyama and T. Fukumoto. *J. Soc. Chem. Ind. Japan*, 42, 489–492 (1939).—Samples in in form of thin flat plates of thickness about 100 μ were made of silver bromide by fusing and leaving it to cool and crystallise between two perfectly flat surfaces of two pieces of pyrex glass. They were well annealed, all in the dark room. Two fine wires of gold, were imbedded in the samples previously, and a strip of area, 1 mm by 10 mm, was made for the measurement of electrice onductance. As the conductance was small, a system of the balanced d.c. amplification was arranged for the amplification of the small current. The spectral distribution of the photoconductance was detd., either in the case of silver bromide alone, or in the cases of silver bromide sensitized with sensitizer dyes. The spectral distribution of energy of this optical system at the place of the sample had previously been detd. by the thermopile. In the case of silver bromide without dyes, the photo-conductance was max. at 454~458 mμ, and the spectral distribution of photo-conductance corresponded well with the photographical sensitivity. In the case of erythrosin, a photo-conductance range with the max. at 560 mμ was found, besides the usual pure silver bromide range. This corresponded well to the photographic sensitivity. The correspondence of the spectral ranges of the photographic sensitivity and the photo-conductance were also found in cases of kryptocyanine and dicyanine. In the former the max. of the photo-conductance was at 745 mμ and in the latter the maxima were at 670 mμ and 568 mμ, besides the usual one of silver bromide. From these facts the authors conclude that electrons are set free or, in other words, elevated to the conduction band by the energy absorbed by the adsorbed sensitizer-dyes, and this is the origin of the latent image due to the dye-sensitization. In the expts. using kryptocyanine, although that amt. of light of 735 mμ which corresponded at least to two quanta for each ion of Br^- and Ag^+ on the surface had been thrown upon the sample, the degree of the photo-conductance did not show any sign of decrease. Although several investigators have shown that one molecule of sensitizer dye is adsorbed for every ten or more of Ag^+ or Br^- ions on the surface, the above result would indicate that the dye is not destroyed after the absorption of light, that is, the function of the sensitizer dye is the transmitter of energy. Authors.

170. **The kinetics of the hydrogenation of ethylene with nickel. II.** O. Toyama. This Journal, 12, 115–124 (1938).

171. **Emission spectrum of the flame of bromine burning in hydrogen and mechanism of the reaction.** T. Kitagawa. This Journal 12, 135–147 (1938).

172. **On the photochemical decomposition of ammonia.** S. Shida. This Journal, 13, 12–30 (1939).

173. **Emission spectrum of the oxy-hydrogen flame and its reaction mechanism. I. Formation of the activated water molecule in higher vibrational states.** T. Kitagawa. This Journal 13, 96–107 (1939).

3—ELECTROCHEMISTRY AND THERMOCHEMISTRY

174. The vapour pressures of both heavy and light hydrates of $BaCl_2$. M. Homma and T. Takai. *Bull. Inst. Phys. Chem. Research.*, **17**, 331—337 (1938).—The dissocn. vapour press. of $BaCl_2 \cdot 2H_2O \rightleftarrows BaCl_2 \cdot H_2O + H_2O$ and $BaCl_2 \cdot 2D_2O \rightleftarrows BaCl_2 \cdot D_2O + D_2O$ were measured in the temp. range 25°—55° by means of a tensimeter. The former reaction was expressed by $\log p_{mm.} = -2.995/T + 10.8129$ and the latter by $\log p_{mm.} = -3,102.5/T + 11.135$. The ratio of both dissocn. press. approached 1 with rising temp. as 1.10 (25°), 1.04 (35°), 1.03 (45°) and 1.01 (55°). From these results $\Delta F°$ and ΔH of hydration by water were calcd. and compared.

J.C.L.

175. Free energy of the formation of aqueous solutions of salts. VI. Free energy of the formation of aqueous soln. of Na_2SO_4 and K_2SO_4. T. Takai. *Bull. Inst. Phys. Chem. Research*, **17**, 338—341 (1938).—Combining the values of the differential free energies of the dissoln. of Na_2SO_4 (anhydrate) in Na_2SO_4 solns. of various concns. calcd. by Sibata, Murata and Toyoda, and those of K_2SO_4 in K_2SO_4 solns. by Murata with those of dilution calcd. from the vapour press. of Na_2SO_4 and K_2SO_4 solns. by Pearce and Eckstrom, the values of integral free energy of dissolution of Na_2SO_4 and K_2SO_4 at 25° were calcd. J.C.L.

176. The chemical equilibrium in the heterogeneous system $MgO(s) + Cl_2(g) \rightleftarrows MgCl_2(s) + \frac{1}{2} O_2(g)$ at high temps. K. Nakazima and T. Okuno. *Tech. Repts. Kyushu Imp. Univ.*, **13**, 49—56 (1938).—The equil. consts. of the reversible reaction, $MgO(s) + Cl_2 \rightleftarrows MgCl_2(s) + \frac{1}{2} O_2(g)$, at 550°, 600°, 650° and 700°C. were statically measured and the numerical values kinetically obtained from these consts. were compared with those of other investigators. The results obtained by the authors are as follows:

$$\log Kp' = 1.7036 - 1,218/T$$
$$\Delta F° = -9,570 - 4.95T \ln T + 0.00025T^2 + 45.69T$$
$$\Delta F°_{298} = -4,330 \text{ cal.}$$
$$\Delta S_{298} = -12.39 \text{ cal./deg.}$$

J.C.L.

177. On the dissociation pressures of hydrates. IV. Vapour pressures of $MnCl_2 \cdot 4H_2O$ and $MnCl_2 \cdot 2H_2O$. K. Sano. *J. Chem. Soc. Japan*, **59**, 846—848 (1938).—By means of a glass spring manometer, disson. vapour pressures of $MnCl_2 \cdot 4H_2O$ and $MnCl_2 \cdot 2H_2O$ were measured and the relations obtained are as follows:

$MnCl_2 \cdot 4H_2O$:
$\log PH_2O(mm.) = -2,893,810/T + 10.534$
$MuCl_2 \cdot 2H_2O$:
$\log PH_2O(mm.) = -3.098.86/T + 10.373.$

From these results, the free energy is calcd. as follows:

$MnCl_2 \cdot 4H_2O = MnCl_2 \cdot 2H_2O + 2H_2O$:
$\Delta F°_{298} = 5,616$ cal., $\Delta H_{298} = 26,500$ cal.
$MnCl_2 \cdot 2H_2O = MnCl_2 + 2H_2O$:
$\Delta F°_{298} = 7,936$ cal., $\Delta H_{298} = 28,378$ cal.

J.C.L.

178. The Faraday effect and the conductivity of electrolytic solutions. A. Okazaki. *Mem. Ryojun Coll. Eng.* **XII**, 33—43 (1939).—(1) It has been found that the equivalent percentage increments Δ of Verdet's const. ω and the rotation const. $D = \frac{n\omega\lambda^2}{(n^2+2)^2}$ of the solns. of alkali halides have linear relations with the degree of dissociation i or the equivalent conductivity Λ over the concn. range of $m < 6$: $\Delta = B + (A - B)\,i = B + (A - B)\frac{\Lambda}{\Lambda_0}$. (2) By graphical extrapolation to i = 1 or 0, the values of A and B concerning ω and D have been detd. The A-value of an electrolyte may be composed additively of the moduli characteristic of the component ions. (3) The molecular rotations of the salts in dissociated and undissociated states have been evaluated by using the values of A and B.

Author.

179. **The Faraday effect of strong elecrolytes in aqueous solutions. VII. NH_4Cl, $BaCl_2$, $NaNO_3$, KNO_3, Na_2SO_4, $ZnSO_4$ and $NaClO_4$.** A. Okazaki. *Mem. Ryojun Coll. Eng.*, **XII**, 45—60 (1939).—(1) The relation between the magneto-optical rotation and the concn. of the aqu. solns. of NH_4Cl, $BaCl_2$, $NaNO_3$, KNO_3, Na_2SO_4, $ZnSO_4$ and $NaClO_4$ has been studied for D-lines. It has been found that the corrected molecular rotation M[D] of the chlorides decreases with increasing concn. and that of $NaClO_4$ increases slightly, while those of the nitrates and the sulphates are nearly independent of concns. (2) The value of M[D] in dissociated state has been detd. by graphical extrapolation to infinite dilution. By using this value of M[D], the corresponding value of moleculer refractivity R and the ordinary dispersion data, the value of $\frac{e}{m}$ for the dispersion electron, its number per molecule and the wave-length of the absorption band of these electrolytes (except for $NaClO_4$) in dissociated states have been evaluated. Author.

180. **Reduction-equilibrium of FeO in liquid iron by hydrogen.** I. Tajiri and Z. Shibata. *Tetsu-to-Hagane*, 25, 194—197 (1939).—For the purpose of detg. the chemico-thermodynamical values of FeO at a high temp., which plays the most important rôle in the chem. reaction of the steel-making process, a known mixt. of steam and hydrogen was passed over the liquid iron, heated by a high-frequency induction furnace at a temp. between 1,545°—1,700°C, to establish the equil. :—

$$FeO(\text{in } Fe(l)) + H_2 \rightleftarrows Fe(l) + H_2O(g).$$

And the equil. const. $K=\frac{P_{H_2O}}{P_{H_2}\cdot FeO\%}$ was calcd., where the oxygen content was detd. by the hydrogen-reduction method. From the results, the relation between the equil. const. and temp. is given as follows: $\log K=\frac{6612}{T}-3.55$.....(1). Using equation (1), the equil. const., detd. at each temp., are reduced to the values at the same temp. of 1,600°C., which depend only on the temp. and are independent of the amt. of FeO in liquid iron : FeO in this case behaves as an ideal soln. From eq. (1), $Fe(l)+\frac{1}{2}O_2=FeO$ (% in Fe) $\Delta F^\circ=-29930-2.40T$, $Fe(l)+\frac{1}{2}O_2=FeO(l)$, and $F^\circ=-61046+14.85T$ are given. And the equil. consts. of the following reaction, Fe (in Fe(l)) $+CO \rightleftarrows Fe(l)+CO_2$.....(2) are expressed as follows: $\log\frac{P_{CO_2}}{P_{CO}\cdot FeO\%}=\frac{7978}{T}-4.88$. From the above, equil. consts. at several temps. were calcd. to compare with the exptl. values. Author.

181. **On the thermal conductivities of some binary gas mixtures.** F. Ishikawa and K. Hijikata. *Bull. Inst. Phys. Chem. Research*, **18**, 401—415 (1939).—This work was undertaken with the purpose of making use of a thermal conductivity method of gas analysis in the accurate investigations on chem. problems. In this report the thermal conductivities of two binary systems $CO-H_2$ and N_2-H_2 were investigated. The thermal conductivity of each pure gas was studied in connection with its press. up to nearly 1 atm. The thermal conductivities of the binary systems, mentioned above, were measured at several const. press., and their results discussed. The expts. were carried out be inserting a conductivity wire as one of the arms of the Wheatstone bridge, and by measuring the voltage which is proportional to the current necessary to keep the temp. of the wire const. By this method the composition of the mixt. can easily be detd. accurately, the max. error being less than 0.1%. The effects on the conductivity of the heat loss due to the end cooling, and of the adsorption of hydrogen by the wire were discussed. Authors.

182. **Studies on the antimony metal electrode for pH determination.** M. Tamai. *J. Biochem.*, **29**, 307—318 (1939).—Antimony metal electrode is said to be useful for pH detn. Its potential is related with pH by the following eq.: E=e—d. pH. But the values of e and d, already reported by many authors, are widely different. The author has studied this deviation of e and d, and

has come to the conclusion as follows. The potential of the Sb electrode is not detd. merely by the pH of the soln., but is also influenced more or less (and indeed is always depressed) by the nature and concn. of the acid radical contained in the soln. The depressing action is most intensive in tartaric, m-phosphoric, oxalic and citric acid; sulphuric, phosphoric and nitric acid are less active, while in hydrochloric and acetic acid it is hardly detectable. The depressing action is remarkable in concd. solns. and fades away with dilution, becoming scarcely detectable at 0.0001 mol. These characteristics are thoroughly maintained even when the acid soln. is neutralized partially or totally with alkali, such as NaOH, KOH, $Ca(OH)_2$ or $Ba(OH)_2$. The deviation of e and d is caused by this depressing action of acid radicals. More than this, there are many factors of accidental errors which disturb the reproducibility of the measurement. Author.

183. **Activity coefficient of strong electrolytes in the concentrated solution.** S. Kaneko. *Bull. Electrotech. Lab.*, 3, 419—420 (1939).—From the theory published in the previous report, activity coeff. of strong electrolytes in the concd. soln. is calcd. and the following formula is obtained: $\ln \gamma = -\frac{\varepsilon^2}{DkT} \sum_i \frac{\nu_i z_i^2}{\nu_s} \frac{\varkappa}{1-\varkappa a} + \left(\frac{4}{3}\pi N \nu_s a^3 - \frac{\partial v}{\partial m}\right)\frac{C}{1000} + \ln \frac{C}{m\delta}$, where γ is activity coeff., ε the charge of an electron, D the dielectric const. of the solvent, k Boltzmann's const., T absolute temp., ν_i the number of the i ions in one molecule, ν_s the total number of ions in one molecule, z_i the valency of the i ions, $\varkappa$ the reciprocal of the thickness of ion atm., a the mean diameter of an ion, N Avogadro's number, $\partial v/\partial m$ the partial molal volume of the solute, C concn. of the soln., m molarity, and δ the density of the solvent. Author.

184. **On the theory of fusion.** A. Harasima. *Proc. Phys.-Math. Soc. Japan*, 21, 156—165 (1939).—A study of the partition function and of the equations of state of solid and liquid is made. By assuming the form of mutual potential energy between two adjacent atoms as consisted of a parabolic part (near the equil. position) and a linear part, the author has obtained S-like isotherms as in van der Waal's theory and detd. the melting point by the condition of phase equil. Lindemann's formula is derived and change of density upon fusion is calcd. Further, the thermal pressure in liquid is calcd. and compared with the result which the author has got previously. Author.

185. **On the thermal conductivity of the system H_2-HCl and the equilibrium in the reduction of cuprous chloride by hydrogen.** F. Ishikawa and N. Imamura. *Bull. Inst. Phys. Chem. Research*, 18, 537—547 (1939).—Using a cell with a straight wire the thermal conductivities of H_2 and HCl were measured at 25°, the press. being varied from zero to 700 mm. The thermal conductivity of the binary system, H_2—HCl, was measured at 300, 500, and 700 mm, and the relation between the conductivity and the composition of the mixt. discussed. Using the result mentioned above, the equil. in the reduction of cuprous chloride by hydrogen was studied at 300 mm and 290—400°. The equil. const. may be expressed by $\log K_s = \log p^2_{HCl}/p_{H_2} = -3824/T + 5.399$ (atm. units). The following thermodynamical values were obtained: $2CuCl(s) + H_2(1\ atm.) = 2Cu(s) + 2HCl(1\ atm.)$, $\Delta H = 22964 - 10.74T + 0.00306T^2$, $\Delta F^\circ = 22964 + 24.73T \log T - 0.00306T^2 - 100.69T$. $Cu(s) + 1/2Cl_2(1\ atm.) = CuCl(s)$, $\Delta H_{298^\circ} = -32080$ cal., $\Delta F_{298^\circ} = -28201$ cal., $\Delta S_{298^\circ} = -13.02$ cal/deg. $S_{CuCl} = 21.30$ cal/deg. It was pointed out that these results were in fairly good agreement with the previous report of M. Watanabe. Authors.

186. **Thermo-dynamical studies on chlorides. V. Reduction equilibrium of chromous chloride by hydrogen.** K. Sano. *J. Chem. Soc. Japan*, 59, 937-940 (1938).—By investigation of the reduction equil. of

The Review of Physical Chemistry of Japan Vol. 13f No. 3 (1939)

chromous chloride by hydrogen, the following reaction was obtained :

(1) $CrCl_2+H_2=Cr+2HCl$:

$\log Kp=-10{,}408.156/T+6.748$ (at 893~1,075°K)

(2) $CrCl_2+H_2=Cr+2HCl$:

$\Delta F^\circ = 53{,}359 + 7.86 \ln T - 0.002025 T^2 - 88.879 T$

$\Delta H=53{,}359-7.86 T+0.002025 T^2$

(3) $Cr+Cl_2=CrCl_2$:

$\Delta F^\circ_{298}=85{,}420$ cal., $\Delta H_{298}=94{,}977$ cal.

$\Delta S_{298}=32.07$ E.U.

(4) $S_{298}(CrCl_2)=26.92$ E.U. J.C.L.

187. **The effect of X-ray on various electric potentials.** K. Yosida. *Kyoto Furitsu Ika Daigaku Zassi*. 22, 1128–1132 (1938).—The radiation of X-ray exerts no influence on various potentials, such as the phase boundary potential of mercury and sulphuric acid or formic acid, the potential of a cell consisting of calomel electrode and 0.1 *N* or satd. potassium chloride, and the potential of the standard cadmium cell. J.C.L.

188. **A study of the electrode potentials of metals in aqueous solutions of nitric acid.** Y. Yamamoto. *Bull. Inst. Phys. Chem. Research*. 17, 614–641 (1938).—Various metals, such as Mg, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Sb, Ta, W, Pt, Au, Hg, Pb, Bi, C, Si, haematite, piano wire, 13% Cr stainless steel, 7 : 3 brass, nickrome alloy, etc., were immersed in pure water or various solns. of nitric acid (10 different concns. from 4.5% to 63%) for 20 minutes, and the changes of the potentials of these metals were measured every 15 seconds by means of a valve potentiometer. A satd. calomel electrode was used as the other electrode and the change was expressed by the absolute potential whose standard was the potential of a satd. calomel electrode (+0.525 V). The result observed was: C, Al, Si, Cr, 13% Cr stainless steel, Ta, W, Pt, Au, etc., were hardly or never corroded, while all the rest of samples were corroded. The electrode potentials either rose or fell immediately after the immersion and then gradually became const. Generally speaking, the electrode potentials tended to rise as the concn. of nitric acid became higher, but those of Al, Zn, Mn, Co, Ag, Cd, Sn, Hg, etc., showed the min. for a certain concn. of nitric acid. As soon as the concn. of nitric acid reached to a certain degree, a sudden rise was noticed in the potentials of Fe, piano wire, 13% Cr stainless steel, Ni, nickrome alloy, etc. Pt has the highest potential, +1.6 V, with Au, W, Ta, Mo, Ag, etc. coming in the order, and Mg at the lowest, −0.7 V. The electrode potentials obtained after 20 minutes' immersion were plotted against the atomic numbers. (Those of Mg, Mn, Zn, Cd, Sn, Pd, etc. lie periodically at the lowest.) The degree of the corrosion does not always agree with the fluctuation of the electrode potentials. J.C.L.

189. **A study of the electrode potentials of metals in aqueous solns. of copper nitrate.** Y. Yamamoto. *ibid.*, 680–693 (1938).—By immersing the same metals mentioned in the preceding expt. in 2, 8, 14, and 20% aqueous solns. of $Cu(NO_3)_2$, their absolute potentials were measured. The metals whose surfaces remained unchanged after 20 minutes' immersion are C, Al, Si, Cr, 13% Cr stainless steel, Ta, W, Pt, Au, Hg, etc. All the rest of samples were affected. The electrode potentials rose or fell immediately after the immersion and then gradually became const. The higher the concn. of copper nitrate became, the larger the electrode potentials tended to be. Fe and piano wire gave 2 kinds of potentials, showing sudden changes of the potential, while Cr, Mn, Pb, etc., showed considerably complex changes of the potential. Pt has the highest potential, +1.2 V, Au, Ta, W, Hg, Ag, etc., coming in the order, and Mg at the lowest, −0.7 V. The order of the magnitude of the electrode potentials of these substances is varied more or less according to the concns. of copper nitrate. J.C.L.

190. **Researches on the electric**

boundary layer disturbance. XIV. The biological water elucidated from the view-point of the adsorption and dispersion of electro-magnetic wave. I. S. Ueda and M. Shikata. *J. Electrochem. Assoc. Japan*, 6, 333–336 (1938).—To make clear the form of biological water the authors investigated the absorption and dispersion of electro-magnetic wave in the Kaoliang-liquid paraffin systems of (I) South- and (II) North-Manchukuo growth at 30°–110°C and below 600 of frequency, and compared the dielectric properties. Exptl. Results: (i) The influence of temp. on the loss of dielectricity—In both samples contg. about 6.5% water, tan δ appears not at low temps., but with increasing temp. (at lower temp. in (I) than in (II)). (ii) The influence of the frequency on the loss of dielectricity—Above 90°C the max. of tan δ appears in (I) and (II), but not in the frequency of the present expt. At the same exptl. temp. the max. of tan δ of (I) appears in the higher frequency as compared with that of (II), and, accordingly, the lower the temp. is the longer the relaxation time is. Consideration of the Exptl. Results: From the water contd. in the samples and the type of rotation of dipole in the case when the dipole moment of water is laid in the alternating electric field it is assumed that (II) has more intense affinity to water than (I), i. e., (II) conts. larger amt. of adsorbed water than (I). **II.** *ibid.*, 337–341 (1938).—Using the same samples contg. about 19% water, the similar expt. was carried out at 9°–45°C by means of a specially made low temp. thermostat. Exptl. Results: (i) The influence of temp. on the loss of dielectricity—Each sample reaches the max. of tan δ at a definite temp. below the frequency of 3000. As the frequency is lowered, the max. point moves to the side of low temp. Above the frequency of 3,000, the lower temp. is, the more tan δ decreases and tan δ can not be calcd. from the side of high frequency. As to the max. of tan δ in the case of the same frequency, that of (I) lies on the side of lower temp. (ii) The influence of frequency on the loss of dielectrocity—In the cases of both (I) and (II), below −20°, the max. of tan δ moves to the side of low frequency with decreasing temp., and accordingly the relaxation time becomes longer as the temp. falls. At the same temp, the max. of tan δ of (II) lies on the side of lower frequency as compared with that of (I) and the relaxation time of (II) is longer. Thus the similar conclusion to the preceding report has been drawn. J.C.L.

191. **The electrolytic solution pressure of pure aluminium. I.** I. Igarasi and S. Kodama. *Nippon Kinzoku Gakkai-Si*, 2, 463–466 (1938).—Though it is stated that the standard electrolytic soln. press. *Eh* is 1.33~1.69 V, yet the value observed by Endo and Kanazawa is only 0.78 V. The fact that the observed value is thus far smaller than that calcd. thermo-dynamically may be ascribed to the oxide film produced on the surface of Al. Therefore, the authors measured the press. in question at quite a standstill, using an electrode of such a purity as 99.9964% and in the complete absence of O_2 and obtained *Eh*≒1.26 V. In this case a special attention was paid to the change of the press. for the first several minutes and also to the effect of the gas introduced. As soon as the electrode was immersed in the soln., the press. gradually rose. The introduction of hydrogen raised the press., and that of oxygen caused a sudden fall in the press. and then raised it. J.C.L.

192. **The specific heats of some solid aliphatic acids and their ammonium salts and the atomic heat of nitrogen.** S. Satoh and T. Sogabe. *Sci. Papers Inst. Phys. Chem. Research*, 36, 97–105 (1939).—The mean specific heats of oxalic, succinic, pyrotartaric, and tartaric acids and their ammonium salts were detd. The atomic heat of nitrogen was deduced from the difference between the molecular heats of ammonium salts and their resp. acids. The atomic heat of nitrogen was found to be about 1.8 in some cases, about 6.4 in other cases and generally about 4.2 which does not much

differ from the value 3.5 provisionally detd. from the study of various nitrides. Authors.

193. **The vapour pressure of dissociated water from hydrates. VI. The vapour pressure of dissociation of $MgCl_2 \cdot 4H_2O$ and $MgCl_2 \cdot 2H_2O$.** K. Sano. *J. Chem. Soc. Japan*, **59**, 1145–1149 (1938).—Using the press. guage of *n*-butylphthalate ester, the author measured the press. in question and obtained the following expressions: $MgCl_2 \cdot 4H_2O$: $\log pH_2O = -3.505.577/T + 10.4625$ and $MgCl_2 \cdot 2H_2O$: $\log pH_2O = -3.601.093/T + 9.6130$. J.C.L.

194. **A thermo-dynamical study of chlorides. VIII. The reduction equilibrium of manganese chloride by hydrogen.** K. Sano. *J. Chem. Soc. Japan*, **59**, 1150–1153 (1938).—By the gas circulating method the author calcd. the equil. const. of $MnCl_2 + H_2 = Mn + 2HCl$ at 820~900°K, and obtained $\log Kp = -14,520.7681/T + 7.4678$. Hence the following thermo-dynamical values: $\Delta F° = 70,311 + 6.02\,T \ln T - 0.00175\,T^2 - 77.818\,T$; $\Delta H = 70.311 - 6.02 + 0.00175.T^2$; $\Delta F°_{298} = 57.187$ cal.; $\Delta H_{298} = 68.672$ cal.; $\Delta S_{298} = 38.54$ E.U. The heat of formation and the free energy of formation of $MnCl_2$ are found to be $\Delta H_{298} = -112,450$ cal. and $\Delta F°_{298} = -102,570$ cal. resp. and $S_{298}(MnCl_2) = 27.45$ E.U. J.C.L.

195. **On the magneto-optical properties of potassium iodomercurate solution.** T. Takei, Y. Hosino and T. Osakada. *J. Electrochem. Assoc. Japan*, 7, 186–189 (1939).—The potassium iodomercurate soln. was found to be the most suitable one for making magneto-optical instruments, as the soln. has an extraordinarily high power of magneto-optical rotation. In the paper, the following magneto-optical and phys.-chem. properties of the K_2HgI_4 soln., especially of the satd. water soln. are described. (1) From the data measured by R. Lucas & F. Gallais, the empirical formula between Verdet's const. V and wave-length λ (μ) was derived: $V \frac{0.0315}{\lambda^2 - 0.132}$ (20°C) The Verdet's const. calcd. from this formula was found to show good agreement with the authors' measurements. (2) The variation of Verdet's const. (for D-line) with temp.: $V_{Dt} = 0.148_2 - 0.000072\,(t-20)$. (3) The specific gravity at 20°C: $d_4^{20} = 3.11$. (4) The absorption spectrum was investigated for the satd. soln., 1/10 satd. soln., and 1/100 satd. soln. (5) The transmission of light was at max. at the wave-length 5800 Å (the soln. showed yellow colour). (6) The refractive index at various concn. was measured. For sat. soln., $n_D = 1.719$ (20°C). (7) The corrosion tests for thirteen organic substances and ten metals were carried out. The organic substances were generally resistant, while the metals were very corrosive except nickel and nickel alloys. Authors.

196. **Thermal analysis of the oxidation of sulphites. (I).** H. Matsuyama. This Journal, 12, 168–191 (1938).

4—COLLOID CHEMISTRY AND SURFACE CHEMISTRY

197. **The influence of dryness of samples on the electrokinetic potentials.** K. Kanamaru, T. Takada and K. Maeda. *Sen-iso Kogyo*, **14**, 132–136 (1938).—The electrokinetic potentials of glass and nitrocelluloses with different degrees of dryness in water and alcohol were measured and the influence of dryness, or the presence of the residual solvated layer, on these potentials was examd. from the authors' theory on lyophilic properties. J.C.L.

198. **On the adsorption of ammonia by platinum black.** I. Sano. *J. Chem. Soc. Japan*, **59**, 1399—1406 (1938).—The adsorption velocity and amt. of ammonia by platinum

black subjected to sintering procedure conducted under evacuation at 500°C for 3 hours (and accordingly it may point to platinum sponge) were measured at 0°, 100°, 200°, 300°, 400° and 500°C under 1 atm. press. Each run of the measurements being over, the gas was collected and analyzed; some quantity of a constituent which was not absorbed by dilute sulphuric acid was found in it. In the case where oxygen existing primarily as a surface compd. on platinum was removed previously through reduction with hydrogen, the insoluble constituent above said might be considered to be the mixt. of hydrogen and nitrogen resulting from the decomposition of ammonia, this appearing at 400°C and upwards; in the case where not treated with hydrogen in advance, it might be nitrogen which manifests itself at 0°C and upwards. It was indicated from calcn. based on these facts that ammonia might be adsorbed activatedly on platinum at 400°C or more. Author.

199. **On the catalytic decomposition of hydrogen peroxide by colloidal platinum-carbonyl.** I. Sano. *Bull. Chem. Soc. Japan*, 13, 118—126 (1938).—The catalytic decomposition of hydrogen peroxide by colloidal platinum-carbonyl as well as colloidal platinum obtainable from it was examd. In the former case, the reaction proceeds as unimolecular after it passed through an induction period; in the latter case, it deviates from unimolecular throughout the course of the reaction concerned, and this may be explained to be due to the retarding influence of oxygen evolved from hydrogen peroxide and adsorbed on the surface of colloidal platinum. Some considerations were made on these facts. Author.

200. **The sorption of gases on reduced nickel. I. Hydrogen, oxygen, and hydrogen bromide.** M. Takebayashi. *Bull. Chem. Soc. Japan*, 14, 47—53(1939).—Y. Urushibara and the present author have found that reduced nickel and reduced iron reverse the direction of the addition of HBr to ethenoid compds. in the same way as oxygen. The expts. are by no means intended for an exact investigation of the sorption itself, but have been carried out with a view to knowing the behaviours of reduced nickel toward these gaseous substances. At 20°, oxygen was more rapidly and abundantly sorbed than hydrogen. The sorbed hydrogen was desorbed in vacuum, whereas the sorbed oxygen was not. The whole oxygen sorbed is considered to be chemically bound to the nickel, and the oxygen was partly removed from the nickel by hydrogen. In the dark, HBr was sorbed gradually and extensively, suggesting an activated adsorption. Reduced nickel, saturated with oxygen, consumed much more HBr. It is supposed that traces of water formed by the action of HBr on the oxygen-stained nickel accelerate the reaction of metallic nickel and HBr to give hydrogen and nickel dibromide. Author.

201. **On the nature of foam. V. Phase inversion and foam formation of emulsion consisting of acetic acid, benzene, and water.** T. Sasaki. *Bull. Chem. Soc. Japan*, 14, 107—114 (1939).—The heterogeneous region of the system consisting of acetic acid, benzene and water (ABW) is divided into three regions A, B and C, referring to the type of emulsion produced by two different modes of shaking. Systems in region A and B produce water-in-oil and oil-in-water emulsion resp. whatever the mode of shaking, and those in region C occasionally produce both types of emulsion according to the two modes of shaking. The region C is called the phase inversion zone by shaking. Some systems of thir phase inversion zone behave both foamy and non foamy according to the two different modes of shaking. The existence of such foam-nonfoam system is restricted in a portion of the phase inversion zone which at the same time forms a portion of foamy region of heterogeneous system of ABW. The difference in nature or behaviour between two possible types of emulsions produced by one and the same system was compared in details, and its discussions were made. Author.

The Review of Physical Chemistry of Japan Vol. 13f No. 3 (1939)

202. **The colloid-chemical studies on systems of three-liquid components. III. On the emulsification between two inmiscible liquids with equal specific gravity.** N. Sata and H. Okuyama. *Bull. Chem. Soc. Japan*, **14**, 135—139 and 147—152 (1939).—It was studied the emulsification between two inmiscible liquids, whose specific gravity exactly the same. Such system of liquid could be prepd. from combination of three liquids with different miscibility and different specific gravity. It was treated the systems: Benzene-Water-Carbontetrachloride, Benzene-Chloroform-Amylalcohol (iso), and Benzene-Methanol-Water. At adequate concn., they gave two-liquid-system with equal specific gravity. Emulsification and coagulation in such systems were related with interfacial tension, viscosity etc., besides their specific gravity. An expt. was carried out, which concerned especially to emulsion-type. The influence of gas-phase and vessel-wall were shown to be the important factors. The The emulsification with ultrasonic wave (450 K.C.) was also studied, which gave almost the same results as other researches, with ordinary two-liquid-systems of different specific gravity. Authors.

203. **Bubbling method of electrosmosis measurement.** H. Muraoka and T. Ōmori. *Bull. Electrotech. Lab.*, **3**, 414—417 (1939).—For a measurement of the velocity of electrosmotic flow by moving of a bubble in the side tube of the Briggs' app., the suitable size of the bubble was observed to be as large as 1.11 times of the diameter of the tube, in which the bubble was situated. By this method, the velocity of electrosmosis was decreased first rapidly, then very slowly and finally was const. with increasing of the thickness of the membrane, the current or voltage being adjusted to be const. A new app. for an ultramicroscopical and electrophoretic method using a bubble was proposed. Authors.

204. **On the catalytic decomposition of oxalic acid by colloidal platinum-carbonyl.** I. Sano, *Bull. Chem. Soc. Japan*, **14**, 121—131 (1939).—The decompn. of aq. solns. of oxalic acid (0.10, 0.05, 0.025 N) due to oxidation accelerated by colloidal platinum-carbonyl of red colour as well as colloidal platinum of black colour obtainable from it was, in the presence of oxygen and diffused day-light, studied during a period extending several hundred hours at 25.0°C. and thirty hours at 50.0°C. In the case where the red sol is added as catalyst, the reaction proceeds as unimolecular after it passed through an induction period and subsequently a transition period, while in the case where the black sol is added, it proceeds as the above after a transition period, no induction period presenting itself. The more dilute the acid soln., the more stable is the sol throughout the course of the expt. and consequently, the larger is the velocity const. It was shown that the reaction should be retarded if cut off from the supply of oxygen. The mechanism of the reaction was discussed on these facts. Author.

205. **On the sorption of phosphorus trichloride by active charcoal.** K. Arii, M. Kawabata and T. Takai. *Bull. Inst. Phys. Chem. Research*, **18**, 356—367 (1939).—The sorption of phosphorus trichloride by sugar charcoal activated by heating at 900° for 2 hours, has been detd. by a static method. The instrument used for the measurements was an all-glass app. which contains Jackson's glass spring manometer and McBain's quartz spring balance. The sorption isotherms, which have been detd. at 20°, 30°, and 50° over a range of press. below one atm., are in good agreement with Freundlich's eq. and the following eqs. are derived from the exptl. data: $a_{20°}=22.945\ p^{0.255}$, $a_{30°}=16.260\ p^{0.2540}$, $a_{50°}=6.427\ p^{0.3100}$. Here, a is the sorption amt. expressed in mg per 1 g charcoal, and p is the equil. press. in cmHg. The empirical eqs. for the isostere are calcd. as follows: $\log p_{20}=18.6691-\frac{5\,550}{T}$, $\log p_{30}=16.7779-\frac{4\,767}{T}$, $\log p_{40}=15.4550-\frac{4217}{T}$. The em-

pirical eq. for the isobar, $a=a_0-x_1t$, where a_0 is the amt. sorbed at 0° and x_1 is the const., is obtained. The values of a_0 calcd. by this eq. can be represented by Freundlich's eq., $a_0=34.120\ p^{0.2065}$. Thus the general eq. between a (mg), p (cm), and t (°C) can be expressed as follows: $a=a_0-xp^mt$, where $x=0.5735$ and $m=0.15825$. Authors.

206. **On the collodion membranes of graded pores.** S. Komagata. *J. Electrochem. Assoc. Japan*, **6**, 256–261 (1938).—Collodion membranes prepd. by the Elford method under various conditions were used to seperate water fiom iso-propyl alcohol and the relation between the press. of water and the amt. of running water was examd. An expression was derived to show the distribution of the pores with respect to the radius of the cylinder or the width of the slit when the pore is regarded either as cylindrical or as of the type of slit capillary. From this expression and the curve already obtained, the relation between the size of the pores and their number is graphically obtained. In the prepn. of the membrane the addition of water makes the pores larger, while acetic acid makes them smaller. The larger the pores are, the more widely they are distributed. J.C.L.

207. **On the chemisorption of carbon dioxide by reduced iron. II.** K. Kawakita. This Journal, **12**, 105–114 (1938).

208. **On the adsorption of hydrogen on poisoned nickel. Studies at low temperatures.** S. Iijima. This Journal, **12**, 148–155 (1938).

209. **On the adsorption of hydrogen on poisoned nickel. II.** S. Iijima. This Journal, **13**, 1–11 (1939).

210. **On the adsorption of nitrogen on reduced nickel.** S. Iijima. This Journal, **13**, 42–48 (1939).

211. **Thermal analysis of the catalytic action of colloids. I. Catalytic decomposition of hydrogen peroxide by colloidal platinum.** E. Suito. This Journal, **13**, 74–86 (1939).

212. **On the chemisorption of carbon dioxide by reduced iron. III. Thermodynamic consideration of the chemisorption.** K. Kawakita. This Journal, **13**, 87–95 (1939).

213. **The decomposition of ammonia by iron catalyst mixed with Al_2O_3 and K_2O.** R. Kiyama. This Journal, **13**, 125–136 (1939).

214. **The decomposition of ammonia by iron catalyst.** K. Seya. This Journal, **13**, 137–144 (1939).